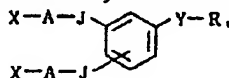


**Title**

Silver halide colour photography photosensitive materials

**Patent Claims**

Silver halide colour photography photosensitive materials characterized in that it contains a coupler with a ballast group represented by the following formula (I).



In the formula, A denotes a coupler residue, X denotes a group which is bonded to the coupler core and is released by performing a coupling reaction to the oxidised compound of the main colour developer, or a hydrogen atom, R1 denotes alkyl group, cycloalkyl group, bridged hydrocarbon compound residue or aryl group, J denotes -CO- or -SO2-, Y denotes -NHCO-, -CONH- or -NHSO2-.

**Detailed Description of the Invention****Technical Field of the Invention**

This invention relates to silver halide colour photography photosensitive materials containing a coupler which has a ballast group.

**Prior Art**

In the field of photographic technique, an image is generally formed by the coupling reaction of the silver halide developer (namely an oxidised primary aromatic amine developer) and a colour-forming compound generally called a 'coupler'. The dye formed by coupling, depending on the chemical composition of the developer and the coupler, is indoaniline, azomethine, indamine or indophenol dye. In colour photography photosensitive materials, the colour formed by the subtractive colour process is usually used, and the obtained image-forming dye is the usual cyan, magenta and yellow dye. These are formed in the sensitive silver halide layer (namely, silver halide emulsion sensitive to red, green and blue radiation) or in contact with these, by radiation which forms the colour complementary to the radiation which the image-formation dyes absorb.

This is a technology which has developed satisfactorily, and so numerous patents and technical reports are known in relation to the chemicals which can be used as couplers to form a photographic image. Couplers which are desirable to form a cyan dye by reaction

with an oxidized colour-formation developer are phenols and naphthols. Representatives of these colour-developing agents are cited in the specifications of US2,772,162, US2,895,826, US3,002,836, US3,034,892, US2,474,293, US2,423,730, US2,367,531, US3,041,236, and in 'Developers - literature - summary' [published in Agfa reports, Vol 2, pp156-175, (1961)].

Couplers which are desirable to form a magenta dye by reaction with an oxidized colour-formation developer are pyrazolone, pyrazolotriazole, pyrazolobenzimidazole and indazolone. Representatives of these couplers are cited in the specifications of US2,600,788, US2,369,489, US2,343,703, US2,311,082, US2,673,801, US3,152,896, US3,519,429, US3,061,432, US3,062,653, US3,725,067, US2,908,573, and in 'Developers - literature - summary' [published in Agfa reports, Vol 2, pp126-156, (1961)].

Couplers which are desirable to form a yellow dye by reaction with an oxidized colour-formation developer are acylacetanilide, for example benzoylacetanilide and pivalylacetanilide. Representatives of these couplers are cited in the specifications of US2,875,057, US2,407,210, US3,265,506, US2,298,443, US3,048,194, US3,447,928, and in 'Developers - literature - summary' [published in Agfa reports, Vol 2, pp112-126, (1961)].

There are also couplers which form a black dye or colourless (neutral) dye by reaction with an oxidized colour-formation developer. Representatives of these couplers are resorcinol and m-aminophenol and the like. These cited in for example the specifications of US1,939,231, US2,181,944, US2,333,106, US4,126,461, and DE2,644,194 and DE2,650,764.

Compounds are also known with the same form as couplers, and which react with oxidized developers, but do not form dyes. These kinds of compound are used to correct the coloured image, by competing with the dye-forming coupler in the reaction with oxidized colour developer, or by releasing a photographic processing agent such as development inhibitor as a result of the coupling reaction. Many of these compounds are not generally called 'couplers', but regarded from the point of view of the form in which these compounds react in photographic processing, they are analogous to couplers, and it is desirable to regard these compounds as couplers. In this invention, these compounds are regarded as couplers. Representatives of such couplers are cited in the specifications of US3,632,345, US3,928,041, US3,938,996, US3,958,993, US3,961,959, US4,010,035, US4,029,503, US4,046,574, US4,049,455, US4,052,213, US4,063,950, US4,074,021,

US4,121,934, US4,157,916, US4,171,223, US4,186,012 and US4,187,110, GB1,445,797, GB1,504,094, GB1,536,341, and GB2,032,914A, DE2,448,063, DE2,552,505, DE2,610,546 and DE2,617,310, and BE839,083.

When a coupler is included in photographic constituents, the coupler is generally dispersed in the photographic constituents by supplement of a high boiling point solvent, called a developer aid. By including a group called a ballast group in the coupler molecule, the coupler becomes non-diffusing, and becomes soluble in the developer aid. This ballast group is present at a site other than the coupling position on the coupler, and provides the coupler with sufficient bulk to cover the coupler and make it non-diffusible in the photographic constituents in processing. It is inferred that the properties and dimensions of the ballast group depend on the bulk of the coupler in the absence of the ballast group, and whether or not other substituents are present.

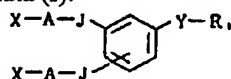
There are many couplers known in this field of technology, but there are usually technical problems with improving the characteristics of many of the couplers and the dyes obtained from them, or in making the most suitable ones in characteristic use coupler and the obtained dyes.

#### Object of the Invention

The object of this invention is to put forward silver halide colour photography photosensitive materials containing a coupler which has a ballast group with extremely improved solubility with respect to the high boiling point organic solvent as a developer aid.

#### Construction of the Invention

The aforesaid object of this invention is achieved by providing silver halide colour photography photosensitive materials containing a coupler with a ballast group represented by the following formula (I).

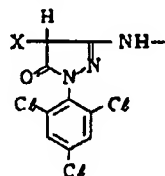


In the formula, A denotes a coupler residue, X denotes a group which is bonded to the coupler core and is released by performing a coupling reaction to the oxidised compound of the main colour developer, or a hydrogen atom, R1 denotes alkyl group, cycloalkyl group, bridged hydrocarbon compound residue or aryl group, J denotes -CO- or -SO2-, Y denotes -NHCO-, -CONH- or -NHSO2-.

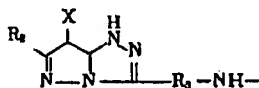
Embodiment of this Invention

The coupler residue represented by A in the aforesaid formula (I) is preferably the residue of a magenta coupler. More preferably, X-A- in the aforesaid formula (I) is one represented by formula (II), (III) or (IV).

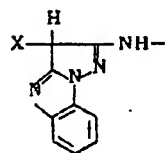
-Formula (II)



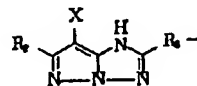
-Formula (III)



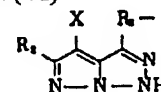
Formula (IV)



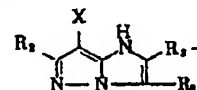
-Formula (V)



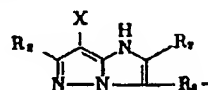
Formula (VI)



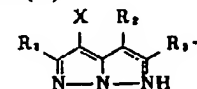
Formula (VII)



Formula (VIII)



Formula (X)



The two R2s in formulae (VI)-(IX) may be the same or different.

In the formula, R2 denotes halogen atom, alkyl group, alkenyl group, alkynyl group, cycloalkyl group, cycloalkenyl group, aryl group, acyl group, sulphonyl group, sulfinyl group, phosphonyl group, carbamoyl group, sulphonamoyl group, spiro compound residue, bridged hydrocarbon compound residue, alkoxy group, aryloxy group, heterocyclyl oxy group, siloxy group, acyloxy group, carbamoyloxy group, amino group, acylamino group, sulphonamido group, imido group, ureido group, sulphonamylamino group, alkoxycarbonylamino group, aryloxycarbonylamino group, alkoxycarbonyl group, aryloxycarbonyl group, alkylthio group, arylthio group or heterocyclylthio group, R3 denotes alkylene group, alkenylene group, alkynylene group, cycloalkylene group, or cycloalkenylene group or the like.

In formula (II)-(IX), the halogen atom denoted by R2 may be for example chlorine atom, bromine atom, particularly chlorine atom.

The alkyl group denoted by R2, for example, preferably has 1-32C, the alkenyl group, alkynyl group, have 2-32C, the cycloalkyl group, cycloalkenyl group has 3-12C, particularly 5-7C, moreover the alkyl group, alkenyl group, alkynyl group may be linear or branched. Moreover, the alkyl group, alkenyl group, alkynyl group, cycloalkyl group, cycloalkenyl group may have substituents [for example aryl, cyano, halogen atom, heterocycle, cycloalkyl, cycloalkenyl, spiro compound residue, bridged hydrocarbon compound residue, and in addition, ones substituted via carbonyl group such as acyl, carboxy, carbamoyl, alkoxy carbonyl, aryloxy carbonyl, furthermore, ones substituted via a heteroatom {specifically ones substituted via an oxygen atom, such as hydroxy, alkoxy, aryloxy, heterocyclyloxy, siloxy, acyloxy, carbamoyloxy and the like, ones substituted via a nitrogen atom, such as nitro, amino (including dialkylamino and the like), sulphamoylamino, alkoxy carbonylamino, aryloxy carbonylamino, acylamino, sulphonamido, imido, ureido and the like, ones substituted via a sulphur atom, such as alkylthio, arylthio, heterocyclylthio, sulphonyl, sulphinyl, sulphamoyl and the like, and ones substituted via a phosphorus atom, such as phosphonyl, and the like}].

Specifically, for example methyl group, ethyl group, isopropyl group, t-butyl group, pentadecyl group, heptadecyl group, 1-hexylnonyl group, 1,1'-dipentylnonyl group, 2-chloro-t-butyl group, trifluoromethyl group, 1-ethoxytridecyl group, 1-methoxyisopropyl group, methanesulphonyl ethyl group, 2,4-di-t-amylphenoxy methyl group, anilino group, 1-phenylisopropyl group, 3-m-butan sulphonylaminophenoxypropyl group, 3-4'-{ $\alpha$ -[4''(p-hydroxybenzenesulphonyl)phenoxy]dodecanoylamino}phenylpropyl group, 3-{4'-[ $\alpha$ -(2'',4''-di-t-amylphenoxy)butanamido]phenyl}-propyl group, 4-[ $\alpha$ -(o-chlorophenoxy)tetradecanamidophenoxy]propyl group, allyl group, cyclopentyl group, cyclohexyl group and the like may be proposed.

The aryl group represented by R2 is preferably phenyl group, and may have a substituent (for example alkyl group, alkoxy group, acylamino group, and the like).

Specifically, phenyl group, 4-t-butylphenyl group, 2,4-di-t-amylphenyl group, 4-tetradecanamidophenyl group, hexadecyloxyphenyl group, 4'[ $\alpha$ -(4''-t-butylphenoxy)tetradecanamido]phenyl group and the like may be proposed.

The heterocyclyl group represented by R2 preferably has 5-7 members, and may be substituted, or may be condensed. Specifically, 2-furyl group, 2-thienyl group, 2-pyrimidinyl group, 2-benzothiazolyl group may be proposed.

As the acyl group represented by R2, for example alkyl carbonyl group such as acetyl group, phenylacetyl group, dodecanoyl group,  $\alpha$ -2,4-di-t-amylphenoxybutanoyl group and the like, aryl carbonyl group such as benzoyl group, 3-pentadecyloxybenzoyl group, p-chlorobenzoyl group and the like may be proposed.

As the sulphonyl group represented by R2, alkyl sulphonyl group such as methylsulphonyl group, dodecylsulphonyl group, and aryl sulphonyl group such as benzene sulphonyl group, p-toluenesulphonyl group and the like may be proposed.

As the sulphinyl group represented by R2, alkylsulfinyl group such as ethylsulphinyl group, octylsulphinyl group, 3-phenoxybutylsulphinyl group and the like, and arylsulphinyl group such as phenyl sulphinyl group, m-pentadecylphenylsulphinyl group and the like may be proposed.

As the phosphonyl group represented by R2, alkylphosphonyl group such as butyloctylphosphonyl group, alkoxyphosphonyl group such as octyloxyphosphonyl group, and the like, aryloxyphosphonyl group such as phenoxyphosphonyl group, and arylphosphonyl group such as phenylphosphonyl and the like may be proposed.

The carbamoyl group represented by R2 may have the alkyl group, aryl group (preferably phenyl group) and the like substituted, and for example N-methylcarbamoyl group, N,N-dibutylcarbamoyl group, N-(2-pentadecyloctylethyl)carbamoyl group, N-ethyl-N-dodecylcarbamoyl group, N-{3-(2,4-di-t-amylphenoxy)propyl}carbamoyl group and the like may be proposed.

The sulphamoyl group represented by R2 may have the alkyl group, aryl group (preferably phenyl group) and the like substituted, and for example N-propylsulphamoyl group, N,BN-diethylsulphamoyl group, N,N-diethylsulphamoyl group, N-(2-pentadecyloxyethyl)sulphamoyl group, N-ethyl-N-dodecylsulphamoyl group, N-phenylsulphamoyl group and the like may be proposed.

As the spiro compound residue represented by R2, for example spiro[3.3]heptan-1-yl and the like may be proposed.

As the bridged hydrocarbon compound residue represented by R2, for example bicyclo[2.2.1]heptan-1-yl, tricyclo[3.3.1.1<sup>3,7</sup>]decan-1-yl, 7,7-dimethyl-bicyclo[2.2.1]heptan-1-yl and the like may be proposed.

The alkoxy group represented by R2 may be one which is substituted further as proposed for the aforesaid alkyl group, for example methoxy group, propoxy group, 2-ethoxyethoxy group, pentadecyloxy group, 2-dodecyloxyethoxy group, phenethyloxyethoxy group. and the like may be proposed.

As the aryloxy group represented by R2, phenyloxy group is preferred and furthermore the aryl core may be substituted by a substituent or atom as proposed for the aforesaid aryl group for example phenoxy group, p-t-butylphenoxy group, m-pentadecylphenoxy group and the like may be proposed.

As the heterocyclyl oxy group represented by R2, one having 5-7 members is preferred and the said heterocyclyl may have further substituents, for example 3,4,5,6-tetrahydropyranyl-2-oxy group, 1-phenyltetrazol-5-oxy group and the like may be proposed.

The siloxy group represented by R2 may be further substituted by alkyl group or the like, for example trimethylsiloxy group, triethylsiloxy group, dimethylbutylsiloxy group and the like may be proposed.

As the acyloxy group represented by R2, for example alkylcarbonyloxy group, aryloxygcarbonyloxy group and the like may be proposed, and may further have substituent, specifically acetyloxy group,  $\alpha$ -chloroacetyloxy group, benzoyloxy group and the like may be proposed.

The carbamoyloxy group represented by R2 may have the alkyl group, aryl group and the like substituted, for example N-ethylcarbamoyl group, N,N-diethylcarbamoyloxy group, N-phenylcarbamoyloxy group and the like may be proposed.

The amino group represented by R2 may be substituted by alkyl group, aryl group (preferably phenyl group) and the like, for example, ethylamino group, anilino group, m-chloroanilino group, 3-pentadecyloxycarbonylanilino group, 2-chloro-5-hexadecanamidoanilino group and the like may be proposed.

As the acylamino group represented by R2, alkyl carbonylamino group, arylcarbonylamino group (preferably phenylcarbonylamino group) and the like may be proposed, and these may have further substituents, specifically acetamido group,  $\alpha$ -ethylpropanamido group, N-phenylacetamido group, dodecanamido group, 2,4-di-t-amylphenoxyacetamido group,  $\alpha$ -3-t-butyl-4-hydroxyphenoxybutanamido group and the like may be proposed.

As the sulphonamido group represented by R2, alkyl sulphonylamino group, arylsulphonylamino group and the like may be proposed, and these may have further substituents. Specifically, methylsulphonylamino group, pentadecylsulphonylamino group, benzenesulphonylamido group, p-toluenesulphonamido group, 2-methoxy-5-t-amylbenzenesulphonamido group and the like may be proposed.

The imido group represented by R2 may be an open chain or a cyclic one, and may have substituent for example succinimido group, 3-heptadecylsuccinimido group, phthalimido group, glutarimido group and the like may be proposed.

The ureido group represented by R2 may be substituted by alkyl group, aryl group (preferably phenyl group), for example N-ethylureido group, N-methyl-N-decylureido group, N-phenylureido group, N-p-tolylureido group and the like may be proposed.

The sulphamoylamino group represented by R2 may be substituted by alkyl group, aryl group (preferably phenyl group), for example N,N-dibutylsulphamoylamino group, N-methylsulphamoylamino group, N-phenylsulphamoylamino group, and the like may be proposed.

As the alkoxy carbonylamino group represented by R2, which may have further substituents, for example methoxycarbonylamino group, methoxyethoxycarbonylamino group, octadecyloxy carbonylamino group and the like may be proposed.

The aryloxy carbonylamino group represented by R2 may have substituent, and for example phenoxy carbonylamino group, 4-methylphenoxy carbonylamino group and the like may be proposed.

The alkoxy carbonyl group represented by R2 may have further substituents, and for example methoxy carbonyl group, butyloxy carbonyl group, dodecyloxy carbonyl group, octadecyloxy carbonyl group, ethoxymethoxy carbonyloxy group, benzyloxy carbonyl



group and the like may be proposed.

The aryloxy carbonyl group represented by R2 may have further substituents, and for example phenoxy carbonyl group, p-chlorophenoxy carbonyl group, m-pentadecyloxyphenoxy carbonyl group and the like may be proposed.

The alkylthio group represented by R2 may have further substituents, and for example ethylthio group, dodecylthio group, octadecylthio group, phenethylthio group, 3-pheoxypropylthio group and the like may be proposed.

The arylthio group represented by R2 is preferably phenylthio and may have further substituents, and for example phenylthio group, p-methoxyphenylthio group, 2-t-octylphenylthio group, 3-octadecylphenylthio group, 2-carboxyphenylthio group, p-acetaminophenyl group and the like may be proposed.

As the heterocyclyl thio group represented by R2, a 5-7 membered heterocyclylthio group is preferred and it may further be a fused ring, and moreover it may have substituents. For example, 2-pyridylthio group, 2-benzothiazolylthio group, 2,4-diphenoxy-1,3,5-triazole-6-thio group may be proposed.

The alkylene represented by R3 preferably has 1-32C, the alkenylene group, alkynylene group have 2-32C, the cycloalkylene group, cycloalkenylene group have 3-12C, particularly 5-7C, moreover the alkylene group, alkenylene group or alkynylene group may be linear or branched.

Moreover, the alkylene group, alkenylene group, alkynylene group, cycloalkylene group, cycloalkenylene group may have substituents [for example aryl, cyano, halogen atom, heterocycle, cycloalkyl, cycloalkenyl, spiro compound residue, bridged hydrocarbon compound residue, and in addition, ones substituted via carbonyl group such as acyl, carboxy, carbamoyl, alkoxycarbonyl, aryloxy carbonyl, furthermore, ones substituted via a heteroatom {specifically ones substituted via an oxygen atom, such as hydroxy, alkoxy, aryloxy, heterocyclyloxy, siloxy, acyloxy, carbamoyloxy and the like, ones substituted via a nitrogen atom, such as nitro, amino (including dialkylamino and the like), sulphamoylamino, alkoxycarbonylamino, aryloxy carbonylamino, acylamino, sulphonamido, imido, ureido and the like, ones substituted via a sulphur atom, such as alkylthio, arylthio, heterocyclylthio, sulphonyl, sulphinyl, sulphamoyl and the like, and ones substituted via a phosphorus atom, such as phosphonyl, and the like}].

Specifically, methylene group, ethylene group, propylene group, isopropylene group, pentadecylene group, cyclohexylene group and the like may be proposed.

As arylene group represented by R<sub>3</sub>, phenylene group is preferred and it may have a substituent (for example alkyl group, alkoxy group, acylamino group and the like).

Specifically, phenylene group, benzylylene group may be proposed.

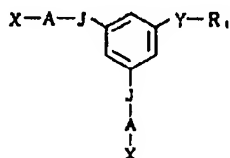
As the group represented by X in formula (I), which is the group that can leave by the coupling reaction with the oxidised form of the colour developer, for example halogen atom (for example fluorine atom, chlorine atom, bromine atom and the like), alkoxy group (for example methoxy group, benzyloxy group and the like), aryloxy group (for example phenoxy group, p-nitrophenoxy group and the like), acyloxy group (for example oxy group (sic) and the like), alkylamino group (for example propylamino group, diethylamino group and the like), aryloxyamino group (for example anilino group, p-hydroxyanilino group and the like), sulphonamido group (for example methylsulphonamido group, phenylsulphonamido group and the like), sulphinamido group (for example phenylsulphinamido group and the like), acylamino group (for example acetylaminogroup, benzoylamino group and the like), alkylthio group (for example tetradecane thio group, benzylthio group, and the like), arylthio group, (for example phenylthio group, 2-naphthoxy-5-octylphenylthio group, p-nitrophenylthio group and the like), alkylsulphinyl group (for example dodecylsulphinyl group and the like), arylsulphinyl group (for example phenylsulphinyl group, p-nitrosulphinyl (sic) group and the like), heterocyclic group (for example pyrazoyl group, succinimido group, pyrrolinyl group, morphoninyl group, piperidyl (sic) group, imidazolyl group, piperidinyl group, hydantoyl group and the like) thiocyano group, sulpho group and the like may be proposed.

X in formula (II), (III) and (IV) is the same as X shown in formula (I).

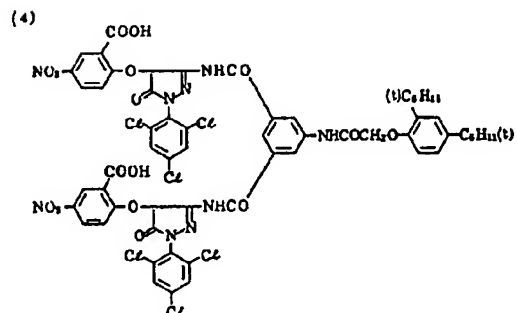
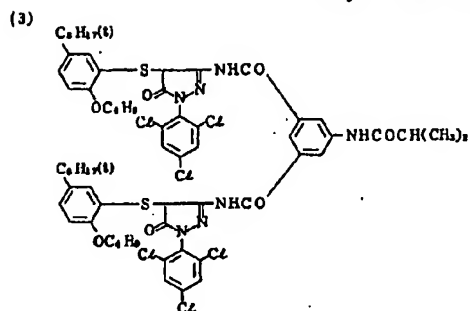
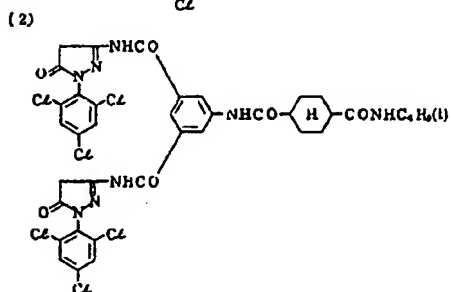
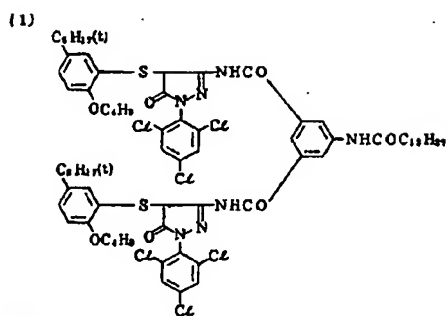
As the alkyl group represented by R<sub>1</sub> in formula (I), one which forms a chain, branch or ring of 1-20C is preferred, for example methyl group, i-propyl group, t-butyl group, dodecyl group, or the like, as cycloalkyl, for example cyclopentyl group, cyclohexyl group and the like, as bridged hydrocarbon compound residue, adamantyl group and the like may be proposed.

As the aryl group represented by R<sub>1</sub>, preferably one which has 6-10C, for example phenyl group, naphthyl group and the like may be proposed. These alkyl groups, aryl groups may each have substituents, and as substituents, for example halogen atom (for example fluorine atom, chlorine atom, bromine atom and the like), cyano group, hydroxy group, alkoxy group (for example methoxy group, ethoxy group, i-butoxy group, dodecyloxy group and the like), aryloxy group (for example phenoxy group, 2,4-di-*t*-pentylphenoxy group and the like), nitro group, amino group, sulpho group, carboxy group, acylamino group, (for example acetylamino group, benzoylamino group, and the like), sulphonamido group (for example methylsulphonamido group, octylsulphonamido gp, benzenesulphonamido group and the like), sulphonamoyl group (for example methylsulphonamoyl group, propylsulphonamoyl group, phenylsulphonamoyl group and the like), hydroxycarbonyl group (for example ethoxycarbonyl group and the like), aryloxy carbonyl group (for example phenoxy carbonyl group and the like), alkylthio group, arylthio group, alkylsulphonyl group, arylsulphonyl group, dialkylamino group and the like may be proposed. There may be two or more of these substituents, and in these circumstances, the substituents may be the same or different.

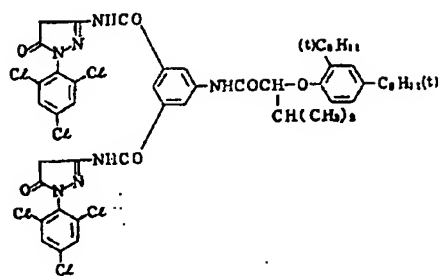
Of the compounds represented by the aforesaid formula (I), ones with the following structure are particularly preferred.



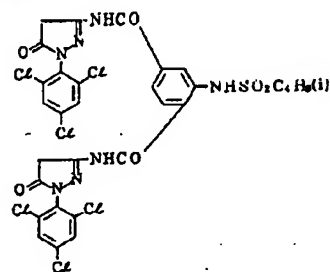
In the following, specific examples of couplers with the ballast group represented by the aforesaid formula (I) are shown, but this invention is not limited to these.



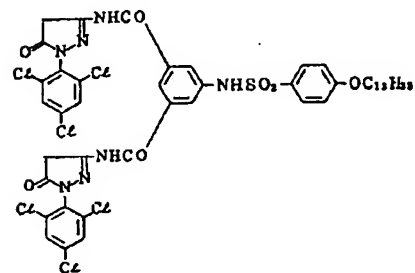
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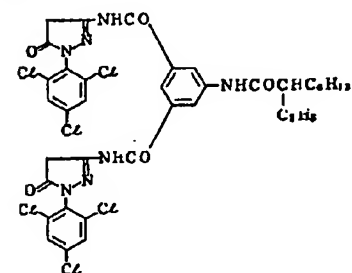
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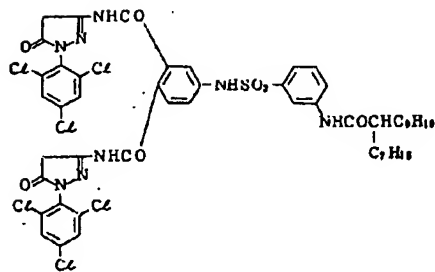
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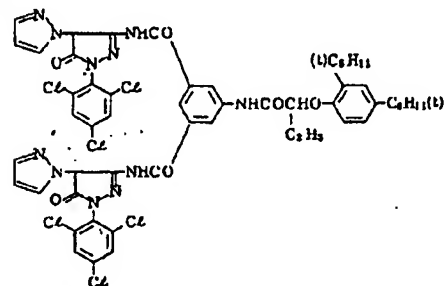
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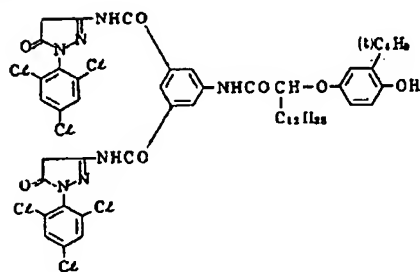
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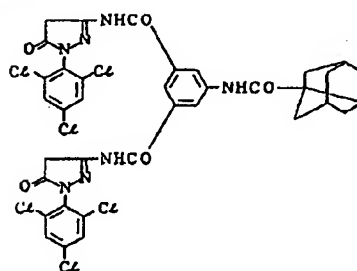
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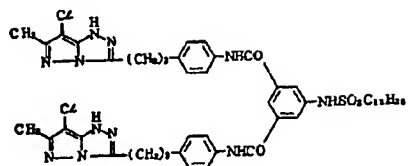
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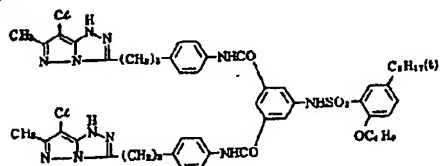
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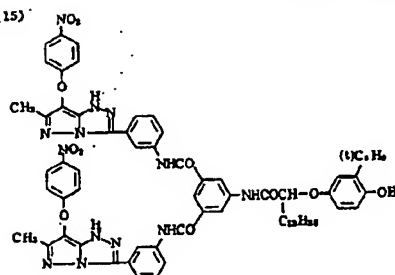
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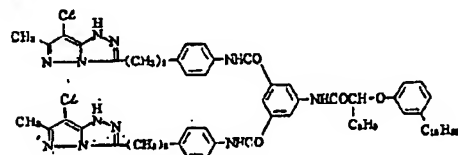
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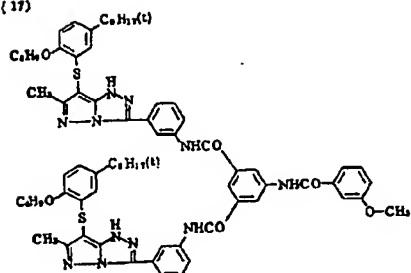
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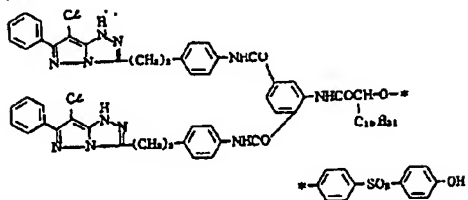
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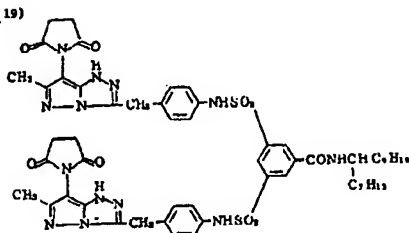
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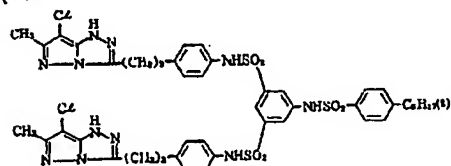
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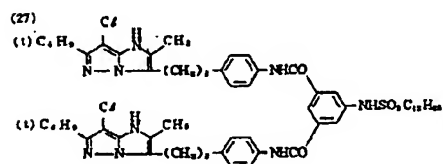
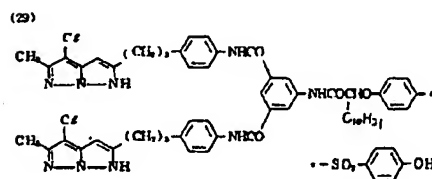
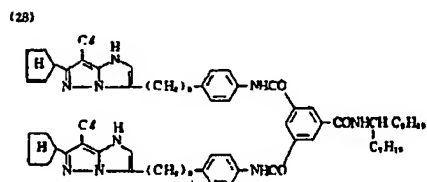
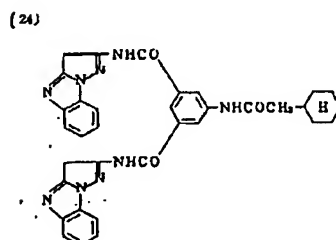
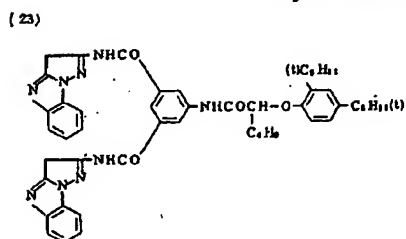


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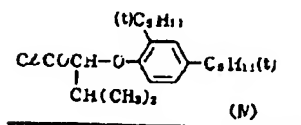
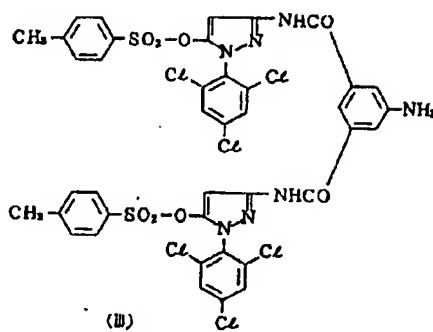
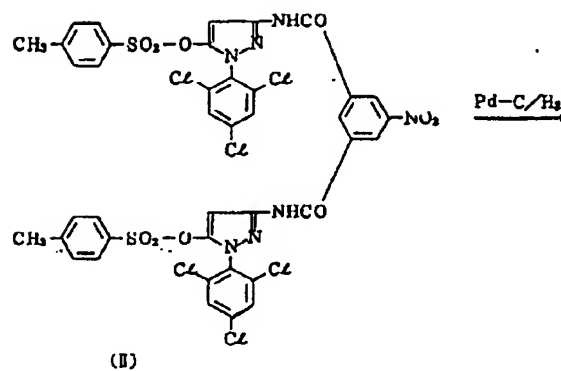
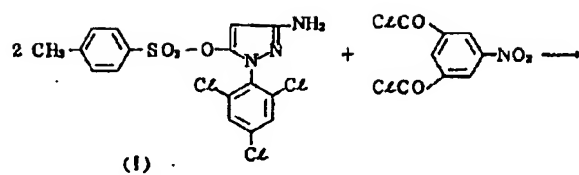


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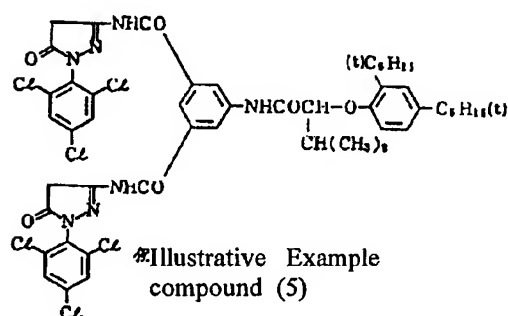
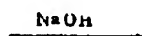
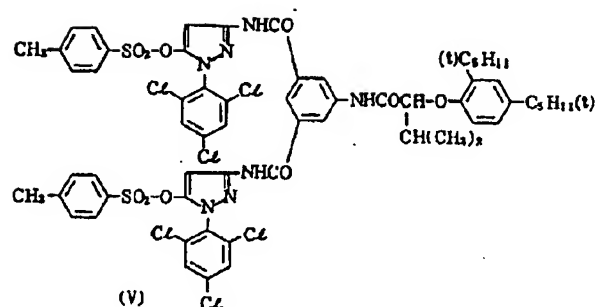




### Reaction scheme.







#### Synthesis of (I)

55.9g (0.20 moles) of 1-(2,4,6-trichloro)phenyl-pyrazol-5-one was added to 560 ml of acetonitrile, and 20.2 g of pyridine was added. 38.2g (0.20 moles) of toluene sulphonic acid chloride was added dropwise, and after 2 hours, the reaction liquor was added to 5 l of water. The precipitated solid was filtered off. The target compound was obtained by recrystallization from 700 ml of ethanol.

#### Synthesis of (II)

21.6g (0.05 moles) of (I) were dissolved in 500 ml of acetonitrile, and 6.3 g of 3-nitro-isophthalic acid chloride was added. After 1 hour, the reaction liquor was added to 2 l of water. The precipitated solid was filtered off, and the target compound was obtained by recrystallization from methanol.

#### Synthesis of (III)

9.8g (0.01 moles) of (II) were dissolved in 800 ml of ethanol, and 1g of palladium-carbon (5%) catalyst was added, and normal pressure hydrogen was applied. The catalyst was filtered off, and reaction liquor was concentrated to about 100 ml, and the crystals were filtered off to obtain the target compound.

Synthesis of (V)

3.0g (0.003 moles) of (III) was dissolved in 100 ml of tetrahydrofuran, and 1.0g (0.003 moles) of (IV) was added dropwise. The reaction liquor was added to 500 ml of water, and it was extracted with ethyl acetate. After concentration, recrystallization was performed with acetonitrile, and the target compound was obtained.

Synthesis of Illustrative Example compound (5)

1.3g (0.001 moles) of (V) was added to 50 ml of ethanol, and furthermore an aqueous solution containing 1.5g of sodium hydroxide was added. After 2 hours, hydrochloric acid was added to the reaction liquor, to neutralize it, and it was added to 600 ml of water. The precipitated crystals were filtered off and recrystallized from a mixture of ethyl acetate and hexane, to obtain the target compound. Confirmation of the target compound was performed from the nuclear magnetic resonance spectrum and the mass spectrum. m.p. was 118-120°C.

The other example compounds were synthesised similarly.

The silver halide photographic sensitive materials of this invention can be, for example, colour negative and positive films, and colour printing paper.

The silver halide colour photographic sensitive materials of this invention can be, for example, colour negative and positive films, and colour printing paper. The silver halide colour photographic sensitive materials of this invention may be for single colour or multiple colour use. When they are multiple colour silver halide colour photographic sensitive materials, in order to perform subtractive colour process redevelopment, there is usually a multi-layer structure of functional layers with a layer sequence which are silver halide emulsion layers, containing each of a magenta, yellow and cyan coupler as coupler, and photosensitive layers, on a support. However, the number of these layers and the layer sequence can be varied, depending on the significant performance and the proposed use.

For the silver halide emulsion used in the silver halide colour photographic sensitive materials of this invention, any of the silver halide emulsions usually used, such as silver bromide, silver iodobromide, silver, iodochloride, silver chlorobromide, silver chloride and the like, may be used.

The silver halide particles used in the silver halide emulsion of this invention may be obtained by any of the acidic method, neutral method, ammonium method and the like. The said particles may be grown for a while, and seed particles may be created and then grown. The process of creating the seed particles and the process of making them grow may be the same or different.

For the silver halide emulsion, the halide ion and the silver ion may be mixed simultaneously, and either one may be mixed in the presence of the other. Moreover, it may be formed while considering the critical growth rate of the silver halide crystals by controlling the pH and pAg in the mixing vessel of the halide ion and the silver ion and adding simultaneously one by one.

When producing the silver halide emulsion of this invention, the silver halide particle size, particle form, particle size distribution, and particle growth rate can be controlled, if necessary by using a silver halide solvent.

With regard to the silver halide particles used in the silver halide emulsion of this invention, a metal ion can be added and included in the particle interior and/or on the particle surface using a cadmium salt, zinc salt, lead salt, thallium salt, iridium salt or complex, rhodium salt or complex, iron salt or dispersion, in the particle formation step and/or growth step, moreover, a reduction increased sensitivity core may be attached to the interior and/or surface of the particles by placing in a suitable reducing atmosphere.

The silver halide emulsion of this invention may have unnecessary soluble salts removed after completion of silver halide particle growth, or they may be left included. When the said salts are removed, this may be performed based on the methods disclosed in 'Research Disclosure 17643'.

The silver halide particles used in the silver halide emulsion of this invention may be formed from layers which are the same in the interior and the surface, or different.

The silver halide particles used in the silver halide emulsion of this invention may be particles such that the latent image is formed mainly on the surface, or mainly in the interior.

The silver halide particles used in the silver halide emulsion of this invention may have regular crystal forms, and may have irregular crystal form such as spherical and tabular.

These crystals may have any ratio of [1,0,0] plane to [1,1,1] plane. Moreover, they may have complex forms, and they may be mixtures of various forms.

For the silver halide emulsion of this invention, two or more silver halide emulsions formed separately may be mixed and used.

The silver halide emulsion of this invention may be chemically sensitised by normal methods. Namely, a sulphur sensitising process using a chemical which contains sulphur which can react with silver ions, and active gelatin; a selenium sensitising process using a selenium compound; a reduction sensitising process using a reducing compound; a noble metal sensitising process using a compound of a noble metal other than gold; and the like can be used alone or in combination.

The silver halide emulsion of this invention may have its spectral sensitivity in selected wavelengths increased using dyes known in the field of photography as sensitising dyes. A single sensitising dye, or a combination of two or more sensitising dyes, may be used. As well as the sensitising dye, a sensitising agent enhancers which is a dye that does not in itself have a spectral sensitising effect, or a compound which essentially does not absorb in the visible region, may also be included in the emulsion to strengthen the sensitising effect of the the sensitising dye.

In the production stage of the photosensitive materials, a compound known in photography as a fogging inhibitor or stabiliser may be added to the silver halide emulsion of this invention during or after chemical ripening, up to coating of the silver halide emulsion, with the object of maintaining stability of fogging inhibition and/or photographic properties during storage or photographic processing.

As binder (or protective colloid) of the silver halide photographic materials of this invention, it is useful to use gelatin, but in addition to this, hydrophilic colloids of synthetic hydrophilic polymer materials such as gelatin derivative, graft polymer of gelatin to another polymer, protein, starch derivative, cellulose derivative, alone or in combination, may also be used.

The photographic emulsion layer, other hydrophilic colloid layer of the silver halide colour photographic sensitive materials of this invention are made into hard films by crosslinking the binder (or protective colloid) molecules, and using film hardening agent

to increase the film strength, alone or in combination. The film hardening agent is preferably added in an amount which can firm the sensitive material into a hard film in a step which does not require the addition of processing liquid, but it is also possible to add it in a processing liquid.

It is possible to add plasticiser with the object of increasing the softness of the photographic emulsion layer and/or other hydrophilic colloid layer of the silver halide colour photographic sensitive materials of this invention.

A dispersion (latex) of water-insoluble or sparingly soluble synthetic polymer may be included with the object of improving the dimensional stability of the photographic emulsion layer and/or other hydrophilic colloid layer of the silver halide colour photographic sensitive materials of this invention.

A dye-forming coupler is used in the emulsion layer of the silver halide colour photographic materials of this invention, which forms a dye in the colour-forming development processing, by the coupling reaction to the oxidised form of an aromatic primary amine developer (for example p-phenylene diamine derivative and aminophenol derivative and the like). The said dye forming coupler is usually selected so that in each emulsion layer, a dye is formed which absorbs the photosensitive spectral light of the emulsion, and uses a yellow dye-forming coupler in the blue photosensitive emulsion layer, a green dye-forming coupler in the magenta photosensitive emulsion layer, and a red dye-forming coupler in the cyan photosensitive emulsion layer. However, silver halide colour photographic sensitive material may be created using different combinations to the aforesaid, in accordance with the objective.

As the yellow dye forming coupler, an acylacetamide coupler (for example a benzoylacetanilide, pivaloylacetanilide or the like) may be used, as the magenta dye forming coupler, a coupler represented by the aforesaid formula (I) may be used particularly preferably, and other than the coupler of this invention is 5-pyrazolone coupler, pyrazolobenzimidazole coupler, pyrazotriazole, medium chain acylacetonitrile coupler and the like, and as cyan dye forming coupler there is naphthol coupler, phenol coupler and the like.

Moreover, a coloured coupler which has a dye correcting effect, and furthermore a developer inhibitor release coupler may be used in addition, as necessary.

When the coupler of this invention is added to the silver halide emulsion layer, usually, the range added is 0.005-2 moles, preferably 0.03-0.5 moles, per mole of silver halide.

For a hydrophobic compound such as non-essential colour formation coupler which is adsorbed onto the silver halide crystal surface, solid dispersion process, late dispersion process, oil-in-water emulsion dispersion process and the like may be used, and this is suitably selected in accordance with the chemical structure and the like of the hydrophobic compound coupler or the like. In the oil-in-water dispersion process, known methods of the prior art may suitably be used to disperse the hydrophobic coupler compounds and the like, and usually, it is dissolved in a high-boiling organic solvent with bp about 150 °C or more and if necessary also using low bp and/or water-soluble organic solvent, and it is dispersed in a hydrophilic binder such as gelatin aqueous solution using surfactant, using a dispersion means such as mixer, homogenizer, colloid mill, flow jet mill, ultrasonicator or the like; and after emulsion-dispersion, it may be added to the target hydrophilic colloid layer. A step of removing the dispersion liquid or simultaneously removing the dispersion and low-boiling point organic solvent may be introduced.

As the high-boiling organic solvent, an aromatic solvent with bp of 150 °C or more is used which does not react with the oxidised form of the developer, such as phenol derivative, phthalate ester, phosphate ester, citrate ester, benzoate ester, alkylamide, fatty acid ester, trimellitate ester and the like.

Anionic surfactant, nonionic surfactant, cationic surfactant may be used as dispersion aid when dissolving the hydrophobic compound in water by dissolving in low boiling point solvent alone or using high boiling point solvent in addition, and dispersing mechanically or using ultrasound.

Between the emulsion layers (between layers of the same colour sensitivity or different colour sensitivity) of the silver halide colour photographic sensitive materials of this invention, a colour fogging inhibitor is used to prevent the generation of discolouration, deterioration of brightness, and conspicuous graininess, due to transfer of the oxidised form of the developer or electron transfer agent.

The said colour fogging inhibitor may be used in the emulsion layer itself, or an intermediate layer between the adjacent emulsion layers may be provided, and this intermediate layer may be used.

An image stabiliser which inhibits deterioration of the colour image may be used in the silver halide colour photographic sensitive materials of this invention.

A UV absorber may be included in hydrophilic colloid layers such as the intermediate layers, protective layers of the photosensitive materials of this invention, to inhibit fogging due to electric discharge originating from friction of the photosensitive materials, and to inhibit deterioration of the image due to UV.

In the silver halide colour photographic sensitive materials of this invention, addition layers such as filter layer, halation prevention layer, and/or irradiation prevention layers and the like may be provided. In these layers and/or in the emulsion layers, dye may be included which leaches from the colour photosensitive material during development processing, or is bleached.

A matt agent which increases the adjustability, lowering the brightness of photosensitive materials in the silver halide emulsion layers and/or other hydrophilic colloid layers of the silver halide colour photographic sensitive materials of this invention, with the objective of preventing mutual interaction of sensitive materials.

A lubricant may be added to lower the friction of the silver halide colour photographic sensitive materials of this invention.

Static inhibitor may be added to the silver halide colour photographic sensitive materials of this invention, to inhibit electrification. The static inhibitor may be used in the static inhibition agent layer which is on the side of the support which does not have the layers of emulsion, and may be used in the emulsion layer or the protective colloid layer outside the emulsion layer of the side where the emulsion layers are laminated on the support.

Various surfactants are used in the photographic emulsion layers and/or other hydrophilic colloid layers of the silver halide colour photographic sensitive materials of this invention, with the object of improving coatability, inhibiting electrification, improving sliding, dispersing emulsion, inhibiting adhesion, improving photographic characteristics (such as colour development acceleration, hardening, increasing sensitivity and the like) and the like.

The photographic emulsion layer, other layers of silver halide colour photographic

sensitive materials of this invention may be covered with flexible reflective support of paper laminated with baryta layer or  $\alpha$ -olefin polymer and the like, synthetic paper and the like, semisynthetic or synthetic polymer film made of cellulose acetate, polystyrene, polyvinyl chloride, polyethylene terephthalate, polycarbonate, polyamide and the like, and rigid body of glass, metal, ceramic and the like.

The silver halide colour photographic sensitive materials of this invention may be coated on the surface of the support, if necessary after corona discharge, UV irradiation, flame treatment and the like directly or via 1 or more undercoat layers (to improve the adhesion, electrostatic inhibition, dimensional stability, rubbing resistance, hardness, halation inhibition friction properties and/or other properties).

When coating the photographic sensitive materials which used the silver halide emulsion of this invention, a thickener may be used to improve the coatability. As the coating method, extrusion coating and curtain coating of two or more layers simultaneously may be used.

The photosensitive materials of this invention can be exposed using electromagnetic waves of the region of the spectrum to which the emulsion layer formed the photosensitive materials of this invention is sensitive. As light source, any known light sources may be used, such as natural light (daylight), tungsten electric light, fluorescent light, xenon arc light, carbon arc light, xenon flash light, cathode ray tube flying spot, various lasers, light-emitting diode, electron beam, X-ray, gamma-ray,  $\alpha$ -ray, and such-like lights which are released from fluorescent bodies by excitation radiation and the like.

The exposure time of 1 millisecond to 1 second is used with a normal camera, and of course, exposure from as short a time as 1 microsecond can be used, for example using cathode ray tube and xenon lamp, exposure of 100 microseconds to 1 microsecond can be used. The said exposure light may be continuous or intermittent.

The silver halide photographic sensitive materials of this invention can form an image by performing well-known colour development.

The primary amine aromatic colour developer used in colour development in this invention includes ones well-known used in a wide field in various colour photographic processes. These developers include aminophenols and p-phenylene diamine derivatives. These compounds are generally used in the form of salts, for example hydrochlorides or



sulphates, because they are more stable than the free forms. Moreover, these compounds are used at concentration range of about 0.1g-about 30g per 1l of developer liquid, preferably about 1g-about 1.5g.

As aminophenol developers, for example o-aminophenol, p-aminophenol, 5-amino-2-hydroxytoluene, 2-amino-3-hydroxytoluene, 2-hydroxy-3-amino-1,4-dimethylbenzene and the like are included.

Particularly useful primary aromatic amine developers are N,N'-dialkyl-p-phenylenediamine compounds, in which the alkyl group and phenyl group are substituted with arbitrary substituents. Among these, as particularly useful compounds, N,N'-diethyl-p-phenylenediamine hydrochloride, N-methyl-p-phenylenediamine hydrochloride, N,N'-dimethyl-p-phenylenediamine hydrochloride, 2-amino-5-(N-ethyl-N-dodecylamino)-toluene, N-ethyl-N- $\beta$ -methanesulphonamidoethyl-3-methyl-4-aminoaniline sulphate, N-ethyl-N- $\beta$ -hydroxyethylaminoaniline, 4-amino-3-methyl-N,N'-diethylaniline, 4-amino-N-(2-methoxyethyl)-N-ethyl-3-methylaniline-p-toluene sulphonate and the like may be proposed.

In the colour development liquid used in processing of this invention, in addition to the aforesaid primary aromatic amine developers, furthermore, various components which are usually added to developer liquids, for example alkalis such as sodium hydroxide, sodium carbonate, potassium carbonate and the like, alkali sulphite, alkali bisulphite, alkali thiocyanate, alkali halide, benzyl alcohol, water softener, thinner and the like may be included. The pH of this colour developer liquid is usually 7 or more, most usually about 10 to about 13.

In this invention, after colour development processing, it is processed with a processing liquid having fixing ability (for example fixing liquid, bleaching liquid), but when the said liquid having fixing ability is fixing liquid, bleaching processing is performed before that. As the bleaching agent used in the bleaching process, a metal complex of an organic acid is used, and the said metal complex is one which has the effect of oxidizing the silver metal formed by development to return it to silver halide, and simultaneously making the non-colour-forming part of the colour-forming agent generate colour, and its structure is one in which a metal ion such as iron, cobalt, copper and the like is coordinated with an amino-polycarboxylic acid or organic acid such as oxalic acid, citric acid and the like. As the most preferred acid used for forming such a metal complex of organic acid, polycarboxylic acid or aminopolycarboxylic acid is proposed. These

polycarboxylic acid or aminopolycarboxylic acid may be alkali metal salts, ammonium salts or amine salts.

As specific representative examples the following may be proposed.

- [1] ethylene diamine tetraacetic acid
- [2] nitrilotriacetic acid
- [3] iminodiacetic acid
- [4] ethylene diamine tetraacetic acid disodium salt
- [5] ethylene diamine tetraacetic acid tetra(trimethylammonium) salt
- [6] ethylene diamine tetraacetic acid tetrasodium salt
- [7] nitrilotriacetic acid sodium salt

The bleaching solution, bleaching fixing solution used, as well as containing such aforesaid metal complex of organic acid as bleaching agent, may contain various additives. As additive, particularly rehalogenation agent of alkali halide or ammonium halide, for example potassium bromide, sodium bromide, sodium chloride, ammonium bromide and the like, and metal salt, chelating agent and the like are desirable. Moreover, well-known ones added to bleaching liquids, bleaching fixing liquids, such as pH buffering agents such as borate, oxalate, acetate, carbonate, phosphate and the like, alkylamines, polyethylenoxides and the like, can suitably be added.

Furthermore, fixing liquids and bleaching fixing liquids can include sulphite such as ammonium sulphite, potassium sulphite, ammonium bisulphite, potassium bisulphite, sodium bisulphite, ammonium metabisulphite, potassium metabisulphite, sodium metabisulphite and the like, pH buffering agent such as boric acid, borax, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, acetic acid, sodium acetate, ammonium hydroxide and the like, singly or two or more.

When performing processing of this invention while supplementing bleaching fixing supplement to bleaching fixing liquid (bath), thiosulphate salt, thiocyanate salt, or sulphite salt may be included in the said bleaching fixing liquid (bath), and by including these salts in the said bleaching fixing supplementing liquid, they are supplemented in the processing bath.

In this invention, in order to increase the activity of the bleaching fixing liquid, air is blown in to the bleaching fixing bath and the storage tank of the bleaching fixing

supplement liquid as required, or oxygen may be blown in, or a suitable oxygenating agent, such as hydrogen peroxide, bromine oxychloride, persulphate salt and the like, may be added.

### **Examples**

In the following, this invention is explained specifically by examples, but this invention is not limited to these.

#### **Example 1**

The couplers of this invention like those shown in Table 1, and comparison couplers are taken each in 0.1 mole with respect to 1 mole of silver, and 1 times the weight of coupler, or 0.6 times, of tricresyl phosphate (high boiling point organic solvent) and 3 times the weight of ethyl acetate were added, and it was dissolved completely by heating to 60 °C. This was mixed with 1200 ml of 5% gelatin aqueous solution containing 120 ml of 5% aqueous solution of alkanol B (alkyl naphthalene sulphonate, made by Dupont), and emulsified in an ultrasonic disperser. Thereafter, this dispersion was added to 4 kg of green-sensitive silver iodobromide emulsion (containing 6 mol% silver iodide), 120 ml of a 2% solution (water:methanol = 1:1) of 1,2-bis(vinylsulphonyl)ethane was added as film hardener, and coated and dried on a transparent drawn polyester base, to produce test samples 1-1 to 1-9. (Silver coating content 20 mg/100 cm<sup>2</sup>).

#### **Development Processing Stage**

Colour-development liquid	38 °C	3 minutes 15 seconds
Bleaching liquid	38 °C	4 minutes 20 seconds
Water washing	38 °C	3 minutes 15 seconds
Fixing liquid	38 °C	4 minutes 20 seconds
Water washing	38 °C	3 minutes 15 seconds
Stabilising liquid	38 °C	1 minute 30 seconds
Drying	47 °C +/- (sic) 55 °C	16 minutes 30 seconds

In each process, the composition of the processing liquid used was as follows.

#### **Colour Development Liquid Composition**

potassium carbonate	30 g
sodium hydrogen carbonate	2.5g
potassium sulphite	5g
sodium bromide	1.3g

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**Caution : Translation Standard is  
Draft Translation**

potassium iodide	2 mg
hydroxylamine sulphate	2.5g
sodium chloride	0.6g
diethylene triamine pentaacetic acid sodium	2.5g
4-amino-3-methyl-N-ethyl-N-( $\beta$ -hydroxyethyl) aniline sulphate	4.8g
potassium hydroxide	1.2 g

Water was added to make up to 1L , and pH was adjusted to 10.06 using potassium hydroxide or 20% sulphuric acid.

**Bleaching Liquid Composition**

ethylene diamine tetraacetic acid iron ammonium salt	100 g
ethylene diamine tetraacetic acid	10g
ammonium bromide	150g
glacial acetic acid	40 ml
sodium bromate	10g

Water was added to make up to 1L , and pH was adjusted to 3.5 using aqueous ammonia or glacial acetic acid.

**Fixing Liquid Composition**

ammonium thiosulphate	180 g
anhydrous sodium sulphite	12g
sodium metabisulphite	2.5g
disodium ethylene diamine tetraacetate	0.5 g
sodium carbonate	10g

Water was added to make up to 1L.

**Stablizing Liquid Composition**

formalin (37% aqueous solution)	2ml
Konidax (made by Konishiroku Photo Industry Co., Ltd.)	5ml

Water was added to make up to 1L.

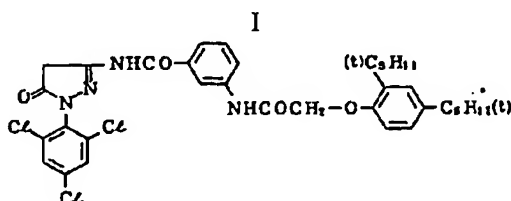
Table 1

Sample No	Coupler used	Maximum density ratio <sup>(1)</sup> %	
		H/C <sup>(2)</sup> = 1.0	H/C <sup>(2)</sup> = 0.6
1-1	comparison coupler (1)	100	100
1-2	" (2)	53	41
1-3	this invention coupler illustrative example (1)	122	134
1-4	" (4)	119	128
1-5	" (5)	122	120
1-6	" (9)	108	122
1-7	" (13)	117	119
1-8	)	118	127
1-9	)	126	135
	" (20)		

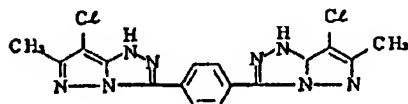
<sup>(1)</sup> Shows the maximum density ratio of the other couplers, taking the maximum density of comparison coupler (1) as 100.

<sup>(2)</sup> H: quantity of high bp organic solvent, C: quantity of coupler (molar quantity) of H/C = 1.0 and H/C = 0.6, the latter has the smaller amount of high bp organic solvent.

Comparison coupler (1)



Comparison coupler (2)



(the compound shown in patent GB1,398,979)

From the results of Table 1, it can be seen that the solubility of couplers of this invention in high bp organic solvents which are colour-forming aids is good, and high maximum density can be obtained.

Example 2

The following development processes were performed using wedge exposure under the same conditions as for samples 1-1 to 1-9 in Example 1. The results are shown in Table 2. Here, the measurement of maximum density ratio was performed by the same method as in Example 1.

Development Processing Stage

Colour-development liquid	38 °C	3 minutes 30 seconds
Bleaching liquid	33 °C	1 minutes 30 seconds
Fixing process or water washing	25-30 °C	3 minutes
Drying	75 °C to 80 °C	2 minutes

In each process, the composition of the processing liquid used was as follows.

Colour Development Liquid

benzyl alcohol	15ml
ethylene glycol	15ml
potassium sulphite	2.0g
potassium bromide	0.7g
sodium chloride	0.2g
potassium carbonate	30.0g
hydroxylamine sulphate	3.0g
polyphosphoric acid (TPPS)	2.5g
3-methyl-4-amino-N-ethyl-N-( $\beta$ -methanesulphonamido ethyl)aniline sulphate	5.5g
potassium hydroxide	2.0g

Water was added to make up to 1L, and pH was adjusted to 10.20.

Bleaching Fixing Liquid

ethylene diamine tetraacetic acid iron (III) ammonium salt dihydrate	60 g
ethylene diamine tetraacetic acid	3g
ammonium thiosulphate (70% solution)	100ml
ammonium sulphite (40% solution)	27.5 ml

pH was adjusted to 7.1 using potassium carbonate or glacial acetic acid, and water was

added to make up to 1L.

#### Stablizing Liquid

5-chloro-2-methyl-4-isothiazolin-3-one	1.0g
ethylene glycol	10g

**Table 2**

Sample No	Coupler used	Maximum density ratio %	
		H/C = 1.0	H/C = 0.6
2-1	comparison coupler (1)	100	100
2-2	“ (2)	49	44
2-3	this invention coupler (1)	109	117
2-4	“ (4)	114	122
2-5	“ (5)	117	132
2-6	“ (9)	108	119
2-7	“ (13)	119	128
2-8	“ (16)	112	130
2-9	“ (20)	123	127

From the results of Table 2, it can be seen that the solubility of samples 2-3 to 2-9 containing couplers of this invention in high bp organic solvents is good, and compared with comparison couplers, higher maximum density can be obtained.

#### Example 3

A multilayer silver halide photosensitive material was produced by coating aqueous gelatin solutions containing the compounds shown in Table 3 on a triacetyl cellulose support, forming layers from the first layer (lowest layer) to the 11th layer (highest layer). Surfactant and gelatin layer hardening agent were added to each layer, in addition to the compound shown in Table 3. This was Sample 3-1.

Samples 3-2 to 3-9 were produced in the same way as Sample 3-1, except that the magenta coupler contained in the sixth layer of Sample 3-1 was replaced as shown in Table 4.

For each sample, the following development processes were performed in a wedge exposure apparatus by normal process. The results are shown in Table 4. Here, the measurement of maximum density ratio was performed by the same method as in

Example 1.

<u>Processing Stage (38 °C)</u>	<u>processing time</u>
First development	6 minutes
First washing	2 minutes
Reversal	2 minutes
Colour development	6 minutes
Adjustment	6 minutes
Bleaching	6 minutes
Fixing	4 minutes
Final washing	4 minutes
Stabilising	30 seconds

In each process, the composition of the processing liquid used was as follows.

#### First Development

pentasodium nitrilo-N,N,N-trimethylenephosphonate	
aqueous solution (45%)	10 ml
potassium sulphite dihydrate	35.0g
sodium bromide	2.2g
sodium thiocyanate	1.0g
potassium iodide	4.5mg
potassium hydroxide	4.5g
diethylene glycol	12.0ml
1-phenyl-4-hydroxymethyl-3pyrazolidone	1.5g
anhydrous potassium carbonate	14.0g
sodium bicarbonate	12.0g
potassium hydroquinone sulphonate	22.0g

Water was added to make up to 1L , and pH was adjusted to 9.6.

#### Reversal Liquid

propionic acid	12.0ml
anhydrous stannous chloride	1.5g
para aminophenol	0.5 mg
sodium hydroxide	5.0mg
pentasodium nitrilo-N,N,N-trimethylenephosphonate	
aqueous solution (45%)	15.0ml



Water was added to make up to 1L , and pH was adjusted to 5.8.

Colour Development Liquid

pentasodium nitrilo-N,N,N-trimethylenephosphonate	
aqueous solution (45%)	5.0 ml
phosphoric acid (85%)	7.0ml
sodium bromide	0.7g
potassium iodide	30.0mg
potassium hydroxide	20.0g
citrazinic acid	1.3g
4-amino-N-ethyl-( $\beta$ -methanesulphonamidoethyl)- m-toluidine sesqui sulphate monohydrate	11.0g
1,8-hydroxy-3,6-dithiaoctane	1.0g

Water was added to make up to 1L , and pH was adjusted to 1.7.

Adjustment Liquid

potassium sulphite	15.0g
ethylenediamine tetraacetic acid	8.0g
$\alpha$ -monothioglycerol	0.5 ml

Water was added to make up to 1L , and pH was adjusted to 6.2.

Bleaching Liquid

potassium nitrate	25.0g
potassium bromide	80.0g
iron (II) ammonium ethylene diamine tetraacetate	110.0g
hydrobromic acid	30.0ml
ethylene diamine tetraacetic acid	4.0 g

Water was added to make up to 1L , and pH was adjusted to 5.7.

Fixing Liquid

ammonium thiosulphate	55.0g
disodium ethylene diamine tetraacetate	0.8 g

sodium metabisulphite

7.5g

sodium hydroxide

1.5g

Water was added to make up to 1L, and the pH was adjusted to 6.6.

Stablizing Liquid Composition

formalin (35% aqueous solution)

6.0ml

Konidax (made by Konishiroku Photo Industry Co., Ltd.)

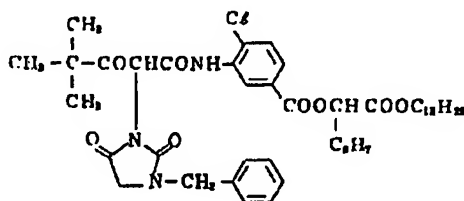
7.5ml

Water was added to make up to 1L.

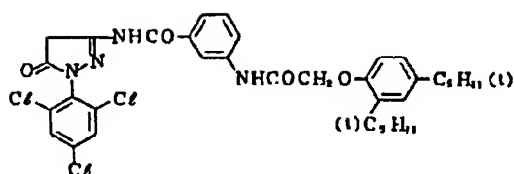
**Table 3**

Layer 11: protective layer	poly methyl methacrylate particles
Layer 10: first blue emulsion layer	silver iodobromide (silver iodide 5.9 mol%) Y coupler 0.06 mol/mol silver
Layer 9: second blue emulsion layer	silver iodobromide (silver iodide 5.9 mol%) Y coupler 0.20 mol/mol silver
Layer 8: yellow filter layer	yellow colloidal silver + 2,5-di-t-octyl hydroquinone emulsion
Layer 7: first green emulsion layer	silver iodobromide (silver iodide 6 mol%) M coupler 0.002 mol/mol silver
Layer 6: second green emulsion layer	silver iodobromide (silver iodide 6 mol%) M coupler 0.006 mol/mol silver
Layer 5: intermediate layer	
Layer 4: first red emulsion layer	silver iodobromide (silver iodide 5.6 mol%) C coupler 0.01 mol/mol silver
Layer 3: second red emulsion layer	silver iodobromide (silver iodide 5.6 mol%) C coupler 0.03 mol/mol silver
Layer 2: intermediate layer	
Layer 1: reflection prevention layer	black colloidal silver
Triacetyl cellulose (support)	

Y coupler



M coupler (comparison coupler 1)



C coupler

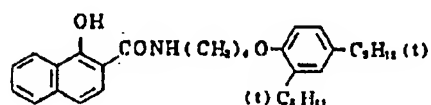


Table 4

Sample No	Coupler used	Maximum density ratio %	
		H/C = 1.0	H/C = 0.6
3-1	comparison coupler (1)	100	100
3-2	" (2)	38	32
3-3	this invention coupler (1)	105	109
3-4	" (2)	107	106
3-5	" (5)	109	106
3-6	" (14)	112	107
3-7	) " (15)	106	108
3-8	) " (19)	110	106
3-9	) " (20)	104	105
	) "		

From the results of Table 4, it can be seen that the solubility of the couplers of this invention in high bp organic solvents is high, and compared with comparison samples, higher maximum density can be obtained.

Example 4

Samples were created by the same process as in Example 1, except that the high-boiling solvent in Example 1 was replaced by dioctyl phthalate, and exposure and development processes were performed in the same way as in Example 1. The results are shown in Table 5.

Table 2

Sample No	Coupler used	Maximum density ratio %	
		H/C = 1.0	H/C = 0.6
4-1	comparison coupler (1)	100	100
4-2	" (2)	39	43
4-3	this invention coupler illustrative example (1)	109	115
4-4	" (2)	113	117
4-5	" (7)	114	113
4-6	" (14)	115	118

From the results of Table 5, it can be seen that even when the high bp organic solvent is changed, the solubility of the couplers of this invention is high, and high maximum density can be obtained.

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